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Assistant Commissioner for Patents,
WASHINGTON, D.C. 20231,

ON November 11, 1999

Rupert B. Hurley Jr.

Rupert B. Hurley Jr.
Registration No. 29,313

November 11, 1999
DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor: Childress et al

Attorney Docket No.: 41933-01

Serial No.: 08/354,177

Group Art Unit: 1761

Filing Date: 12/12/94

Examiner: Tran Lien

Title: HEAT SHRINKABLE FILMS CONTAINING SINGLE SITE
CATALYZED COPOLYMERS

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DECLARATION UNDER 37 CFR 1.132

Assistant Commissioner for Patents
Washington, D.C. 20231

State of South Carolina
County of Spartanburg

I, Blaine Childress, declare as follows:

1. That I received my Bachelor of Science Degree in Textile Chemistry at Auburn University in 1974; and received my Master of Science Degree in Textile Chemistry in 1978;

2. That from 1978 through April 1, 1998 I was employed by the Cryovac Division of W.R. Grace & Co.-Conn. in Duncan, South Carolina as Research Associate; that from April 1, 1998 to the present I have been employed by Cryovac, Inc. My career at Cryovac has included laboratory management including supervision of microscopy, thermal analysis, and spectroscopy. Since 1991 my focus has been in product development in the polymer science group of Research Development, and Engineering.

3. Exxon personnel visited the offices of the Cryovac Division of W.R. Grace & Co., to promote their new line of metallocene-catalyzed linear ethylene/alpha-olefin copolymers, which was a new homogeneous ethylene/alpha-olefin copolymer. These metallocene-catalyzed linear ethylene/alpha olefin resins supplied by Exxon have the same polymer architecture as the linear homogeneous ethylene/alpha olefin resins disclosed in U.S. Patent No. 3,645,992, to Elston ("ELSTON").¹ Exxon indicated these copolymers would be useful in preparing films. Exxon personnel stated that they had prepared blown films from their new metallocene-catalyzed linear homogeneous resins, and found these linear homogeneous resins to operate in a manner similar to linear low density polyethylene ("LLDPE"), but with clarity and strength improvements linked to single-site catalysis. The phrase "homogeneous resin" is synonymous with a resin produced with single site catalyst.

4. Thereafter, I began to examine the Exxon metallocene-catalyzed linear homogeneous ethylene/alpha-olefin copolymer resins for use in preparing heat shrinkable films in an effort to determine whether advantages seen by Exxon in evaluations in blown films could be could be seen in heat shrinkable films. I substituted the Exxon linear homogeneous resins for EVA resins, as well as for heterogeneous LLDPE, in a commercial film formulation using a commercial process. During my initial attempts to use the Exxon resin I quickly realized that the linear resin from Exxon did not operate like LLDPE when attempting to produce heat shrinkable films. For example, a 0.922 g/cc ethylene/hexene linear homogeneous resin from Exxon produced high extruder head

¹ See USPN 5,408,004, more particularly Column 3 lines 43-56.

pressure and low melt strength for all film structures attempted. Attempts to alleviate the high head pressure by raising the extruder temperature further weakened the polymer melt strength, and no quality heat-shrinkable film could be produced. Furthermore, slowing the process rate provided no relief to the problem. Much of the film did not survive the downward tape casting step, and that which did survive resulted in hazy, streaked film. I was surprised at this result due to the advertised excellent optical quality found by Exxon when making blown films and the statements made by Exxon personnel that these Exxon linear homogeneous resins behaved similarly to LLDPE when examined by their staff.

5. I discussed the extrusion performance of the Exxon resins with Mr. Gautam Shah, a Cryovac research and development colleague who had also investigated the performance of the Exxon linear homogeneous resins. Mr. Shah informed me that he too had experienced problems when attempting to extrude the homogeneous resins supplied by Exxon in structures wherein the Exxon resins were designed to serve as major components in a film. Moreover, Mr. Shah stated that the problems persisted even when the Exxon linear homogeneous resin was used in making an upward-blown film, (i.e., in a process quite different from the process used to make a heat-shrinkable film). Therefore, it was felt by both Mr. Shah and me that linear homogeneous resins such as discussed in ELSTON or supplied by Exxon were unsatisfactory for making heat shrinkable films. At this point it seemed clear to me that metallocene-catalyzed resins were not going to meet the initial expectations set by Exxon, and were unsuitable as replacements for LLDPE in preparing commercial heat shrinkable films.

6. Nevertheless, I continued to explore the potential of the new homogeneous resins. I attempted to prepare 2-ply films for use in our heat shrinkable patched bag at one of the U.S. Cryovac factories. Although I continued to experience the undesirable high extruder head pressure, I produced good quality 2-ply film wherein the linear metallocene-catalyzed Exxon resin replaced the ethylene/vinyl acetate (EVA) copolymer within the second layer of a commercial heat shrinkable patch film formulation otherwise in accordance with U.S. Patent No. 4,770,731, to Ferguson ("FERGUSON"). The second

layer of the commercial heat shrinkable patch film made up only 15% of the total film thickness. [See Exhibit F.] Next, I produced good quality film by further replacing the EVA component of the blended first layer of the film. This first layer makes up 85% of the film thickness and is formulated with a blend of 10% EVA, 87% LLDPE and 3% LDPE. Thus, a film could be produced having both EVAs replaced by the Exxon metallocene catalyzed linear homogeneous resin comprising about 23.5% the film structure. [See Exhibit G.]

7. However, when attempts were made to use the linear homogeneous resin to replace the LLDPE component of the commercial heat shrinkable patch in accordance with FERGUSON, no film could be produced. A blend of 10% EVA, 3% antiblock, and 87% of the Exxon linear homogeneous resin in the first layer of the film, did not provide sufficient melt strength to produce the heat shrinkable patch film. The melt strength was unsatisfactory despite slowing the process significantly and lowering the extrusion temperature. [See Exhibit H.] Attempts to salvage the factory experiment by increasing the EVA content of the thicker first layer of the heat shrinkable patch film beyond the level of that of the film of FERGUSON also met with unsatisfactory operability. [See Exhibit J.] Thus, while heat shrinkable films comprising linear homogeneous resins could be produced as modifications to the film formulations taught by FERGUSON, those modifications were limited to designs in which the loading of linear homogeneous ethylene/alpha olefin resin within the film construction did not exceed about 85%. Again, it seemed clear that Exxon's statements regarding their experience in blown films with their new linear homogeneous resins could not be generally applied to the commercial manufacture of heat shrinkable films such as for patch, especially with regard to replacing LLDPE. Indeed, testing with other linear homogeneous resins, wherein the linear homogeneous resin replaced all of the LLDPE as well as all of the EVA in the first layer of the heat-shrinkable patch film, resulted in complete failure. [See Exhibit K.] More particularly, when the resins forming both the first and second layers of the heat shrinkable patch film disclosed in FERGUSON were replaced almost entirely with linear homogeneous resins from Exxon, no film could be produced. [See Exhibit L.] Thus, one of ordinary skill in the art

would have to conduct undue experimentation to determine whether linear homogeneous resins such as those from Exxon *could* be used as replacements for the resins of the heat shrinkable patch films, i.e., as a substitute for the LLDPE in the heat shrinkable patch of FERGUSON. [Again, see Exhibit H, which demonstrates that Exxon linear homogeneous resins are not a suitable "drop-in" for 87% LLDPE when attempting to produce the heat shrinkable patch film formulation of FERGUSON.]

8. After many unsuccessful attempts at using Exxon linear homogeneous resin to produce heat shrinkable films on commercial equipment, I discovered that adding another selected resin, such as high density polyethylene, to a linear homogeneous resin, for instance in an amount of about 15%, could be used to reinforce the melt strength of the deficient linear homogeneous resin, and could allow me to produce heat shrinkable films using linear homogeneous resin. Similarly, I discovered that I could blend 30% low density polyethylene with 70% Exxon linear homogeneous resin to successfully produce heat shrinkable film on commercial equipment. At levels of about 85% of linear homogeneous resin, a reinforcing polymer is required to provide adequate melt strength to the film using the commercial process for making heat shrinkable films, especially those for use as a heat shrinkable patch. In addition to blending with reinforcing materials (materials such as HDPE, LLDPE, LDPE, EVA, etc.), I discovered yet additional ways to repair the deficiencies of linear homogeneous resins, such as the Exxon metallocene catalyzed resin. For example, I could add additional layers to a heat shrinkable patch film construction, and thereby place the melt strength donating material within separate layers to support the film melt curtain during the commercial downward casting step. With such a reinforcing strategy, I was able to make heat shrinkable films comprising linear homogeneous resin in amounts up to about as high as 85%, based on total film weight, using the commercial manufacturing method as otherwise disclosed in FERGUSON. Of course, the need for such reinforcement by blending or multilayer construction was not taught by the disclosure of ELSTON, or by Exxon when discussing blown films, but instead was learned through extensive experimentation.

9. I learned that I could also select a different process than taught by FERGUSON to produce heat shrinkable patch films having high levels of the linear homogeneous resin. For instance, I could extrude film using a flat cast process rather than the downward cast process of FERGUSON, thereby avoiding the melt strength issues associated with the Exxon linear homogeneous resins by way of mechanical support from the casting roller. Surprisingly, if extruding using a horizontal slot die, I could successfully produce a film comprising 100% Exxon linear homogeneous resin, then collect the roll of thick film for solid state orientation using a tenter frame process. However, I reiterate that substitution of the LLDPE component of FERGUSON with a linear homogeneous resin, such as disclosed by ELSTON or supplied by Exxon, is inoperable in the film and process of FERGUSON.

10. The following Table provides a summary of some of my inventive activity discussed above. Note that operability was "YES" for the Control (film of FERGUSON, i.e., Exhibit E), as well as when I used the linear homogeneous copolymer at levels of about 15% and 23½% of the total patch film structure. On the other hand, operability was "MARGINAL" at 82% linear homogeneous copolymer, and operability was "NO" with the highest loadings of linear homogeneous copolymer in the modification to commercial patch film structure using the commercial manufacturing process.

Exhibit	Notebook Page	Operability	Comment
E [Control*]	239360	YES	Control B003 successfully made (87%LLDPE in First Layer)
F	239361	YES	SLP 4008 (0.885 g/cc, 4.0 MI E/H resin) replacing EVA Layer (15% of film structure)

G	239362	YES	SLP 4008 replacing Second Layer; SLP 3011D (0.900 g/cc, 1.0 MI E/H resin) replacing EVA component of First Layer (23½% of total film structure)
H	240416	NO	87% Exxon SLP 402G (0.917 g/cc, 1.1MI, ethylene/hexene resin) in First Layer
J	240414	MARGINAL	82% Exxon SLP 404H (0.928 g/cc, 0.83MI, E/H resin) in First Layer (made with difficulty)
K	240415	NO	First Embodiment: 97% Exxon SLP 402G in First Layer Second Embodiment: 97% Exxon SLP 404H in First Layer
L	239363	NO	SLP 9017 (0.920g/cc, 3.0 MI, ethylene/hexene resin) replacing LLDPE and EVA in First Layer; SLP 4008 replacing EVA in Second Layer

* Film made according to FERGUSON

11. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Further Declarant sayeth not.

Blaine C Childress

Blaine C. Childress

PROBLEM NO.

137-017

DATE

CRYOVAC

SUBJECT: B003 Alternate Resins

This project is a replacement resin for the seal layer. During transition the optics of the bubble became much worse. Also the head pressure and amps increased significantly.

EXHIBIT

F

Extruder & Die Conditions

RDT Conditions

Cold Bath Conditions

Loop	"B"	"C"	Die	Beam 1	Beam 2	KV	Inv. Pos	Variance	Shoe Size	Shoe Length	Shoe Die Dist.	Shoe Air	Water Ring Sec	Water Flow	Water Temp	Inv. Pos.	Variance	Dust Type	Duster Set	Dust Main Air	Dust Stem Air	Dust Vibration	Line Spd Ref.
1	1-200/150	470/125	377/400	21.0	20.3	500	75	85	15.5	15"	5"	80 S.F.	15	35 RPM	42 F			Macro MARK 20	16	70	28	42	82.7
2	2-200/150	475/125	417/400																				
3	3-205/155	485/125	483/400																				
4	4-313/320	373/372	505/400																				
5	5-322/325	374/372	475/400																				
6	6-314/325	410/400	475/400																				

Melt Temp: 345
Head Press: 7500
RPM: 1425
Amps: 12.4

Driven Roll Speeds
Cold Bath 41.1
Infeed In 41.7
Infeed Out 41.5
Infeed Exit 41.2
Over 41.6
Over Exit 45.8
Deflate 154.4
Teg. W.p. 136.6
Long R.R. 3.75
Trans R.R.

Recking Conditions
Steam 213/213
EG Air 260/260
Vertical Air 295/296 Auto
Tape Temp 233/234
Film Temp 181/180
Air Ring % 67.2
Vert Den Sig 1.5
Footage 1000
Taper 1
Tension 40

Line rate was decreased to accommodate the increased head pressure.

Tape Gr. 29.1 Tape Width 15 1/4
Film Gr. 4.50 Film Width 56

A/B/B/ Structure
A: 87.02 LLDPE B: Exxon Exact SLP 400B
10.0% EVA Lot # 90201
3.0% Additive Package

CONFIDENTIAL

SIGNED

DATE

UNDERSTOOD AND
WITNESSED:

DATE

No 239361 B

PROBLEM NO 137-017

DATE

CRYOVAC

SUBJECT: 3003 Alternate Resins

This project is a replacement for EVA which is one of the three components of the outer layer. The replacement resin will be EXXON EXACT SLP 3011D

EXHIBIT

lot No. 90246. The optics are still poor. NOT ANY better than the standard film.

Extruder and Die Conditions

ADI Conditions

Racking Conditions

	"B"	"C"	Die
Loop #1	250/320	437/415	400/400
2	270/320	425/425	420/400
3	322/315	425/425	430/400
4	313/320	374/375	510/400
5	321/325	371/375	475/405
6	312/325	411/400	477/475

Beam 1 - 20.5

Steam

213/343

Beam 2 - 20.3

E.Q. Air

260/300

KV 500

Vert. Air

312

Iuv. Pos

Tape Temp

5/1

Variac 85

Film Temp

181/180

Air Ring %

71

Cold Bath Conditions

Vert. Open Side

1.50

Melt Temp. 249

Shoe Size

15.5

Feed Press. 7500

Shoe Length

15"

R.P.M. 14.5

Shoe/Die Dist.

5"

Amps 181

Shoe A.W.

80

Taper

1

Tension

40

Footage

8600

Driven Roll Speed

Cold Bath 42.8

Water Ring Size

15"

Irradi. IN 43.5

Water flow

35

Irradi. Cut 43.2

Water Temp.

42

Iuv. Exit 44.3

Iuv. Pos

Oven 43.7

Variac 9

Oven Exit 45.4

Duster Set 16

Debate 158.4

Main Air 68

Iso Nips 147.7

Steam Air 28

Vibrator 42

Line Spd Ref. 82.7

cm/dart/100

Long. Racking Ratio

3.72

Trans. Racking Ratio

Tape Ga. 29 Tape Width 15 1/2

A/B//B/A Structure

Film GA 450 Film Width 56

A = 87.0% LLDPE (lot #90246)

B = Exxon Exact SLP

10.0% EXXON EXACT (SLP 3011D)

Lot # 90246

3.0%

CONFIDENTIAL

SIGNED

James H. [Signature]

UNDERSTOOD AND WITNESSED:

[Signature]

DATE

DATE

No 239362 B

PROBLEM NO.

DATE:

SUBJECT: LINE 01 IOWA PARK BOOZ ALT. RBWS

CRYOVAC

⑤ REPLACE LLOPE WITH SLP 402 G

EXHIBIT:

H.

87% SLP 402 G

10% EVA

3% additive package

CONDITIONS SAME AS CONTROL NEGOT 240413

EXT B HP - 5500
MT -
AMPS -
RPM -

EXT C HP -
MT -
AMPS -
RPM -

ZONE 1 - 380
2 - 380
3 - 380
4 - 380

GATE - 380
ADAPTER - 380

COLD BATH -
OVEN -
EXIT -
DEFATE -
ISULATION -

OVEN STEAM -
H₀ -
V₀ -

TAPE TEMP -
FILM TEMP -

RDI
SPEED REF. -
IN -
EXIT -

SEAM 1 -
2 -

TOTAL

LOW MELT STRENGTH - COULD NOT KEEP
TAPE FROM PILING UP ON SHOE - TRIED LOWER
EXTRUDER TEMP PROFILE - SEE ABOVE.

⑥ INCREASE % EVA

82% SLP 402 G

15% EVA

3% Additive Package

SAME PROBLEM AS #5 ABOVE

CONFIDENTIAL

UNDERSTOOD AND
WITNESSED:

Blaine Childress

SIGNED

DATE

DATE

NS 240416 B

PROBLEM NO.

DATE

SUBJECT: LINE 01 IOWA PARK 6002 ALT. RESINS TRIALS

CRYOVAC

② REDUCE LLDPE^W/SLP 404HEXHIBIT
J

BLEND - 82% SLP 404H (0.83 MI)

15% EVA

3% Additive Package

LOWERED LINE SPEED REF. TO 68.8 (40.2 FPM COLD BATH)
ON STANDARD MAT'L BEFORE CHANGE OVER - THIS LOWERED
EXT C HEAD PRESSURE TO 5500 PSI

ALL CONDITIONS SAME AS CONTROL EXCEPT:

EXT B HP - 4600
MT - 257
AMPS - 115
RPM - 12.2

EXT C HP - 7300
MT - 489
AMPS - 359
AAM - 57.0

COLD BATH - 40.3

OVEN - 41.3

EXIT - 47.1

DEWATE - 166

ISOLATION 150

OVEN STEM - 215

HO - 270

VO - 278

TAPE TEMP - 246

FILM TEMP - 179

ROI

SPEED REF - 68.8

AM - 40.6

EXIT - 41.0

BEAM 1 - 24.0

2 - 23.9

6.0 MI

47.4
TOTAL

RATIOS - MD 166/40.3 4.1

TD 525/15.2 3.4

TOTAL 13.94

BUBBLE BROKE AFTER

2020 FT. STABILITY

NOT GREAT - PROBABLY

CAUSED BY FOLD IN TAPE -

TIME FOR HEAT SEAL -

SHRINK 11% x 12% TEST 1
11% x 14% TEST 2

CONFIDENTIAL

SIGNED

UNDERSTOOD AND
WITNESSED:

DATE

DATE

Blaine Children No 240414 B

PROBLEM NO. 122-00

DATE

SUBJECT: LIVE 01 IOWA PARK 8002 ALT RESIN TRIALS

CRYOVAC

(3) REPLACE LLOPE and EVA WITH SLP 404 H

EXHIBIT

97% SLP 404 H (0.83 MI)

3% Additive PKG

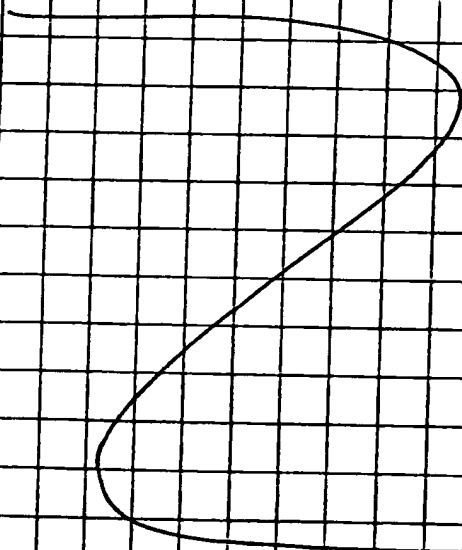
TAPE KEY PILING UP ON SHOE - UNABLE TO RESTART LINE
BEFORE RUNNING OUT OF SLP 404 H.

(4) REPLACE LLOPE AND EVA WITH SLP 402 G

97% SLP 404 G (1.11 MI)

3% Additive PKG

DID NOT ATTEMPT - WOULD NOT RUN WITH
10% EVA - SEE NBPN 240416



CONFIDENTIAL

SIGNED

DATE

UNDERSTOOD AND
WITNESSED:

DATE

Blaine Childress

No 240415 B

PROBLEM NO. 131 JOIT

DATE

July 16, 1972

1972

SUBJECT: 3003 Alternate Resins

This project is a replacement for LLOPE. LLOPE is the base resin for the outer layer blend. The replacement resin will be Exxon Exact JOIT lot # 90239

EXHIBIT

A

Extruder & Die Conditions

ADI conditions

Racking Conditions

Loop #	B	C	Die	Beam 1	Beam 2	NV	Inv. Pos	Variac	Steam	EG Air	Vent. Air	Tape Temp	Film Temp	Airflow	Wind Up Speed	Ther	Tension	Footage
1																		
2																		
3																		
4																		
5																		
6																		

Melt Temp

Head Press.

R.P.M.

Amps

Driven Roll Speeds

Colet Bath

Inner Tow

Inner Out

Tow 2nd

Oven

Oven Ent

Definice

Tow Wps

CB/DeRate

Long R.R.

Trans R.R.

Tape Gr.

Film Gr.

39

Tape Width

Film Width

54

56

A/B/A/A Structure

A/B/A/A Structure

A/B/A/A Structure

A/B/A/A Structure

A/B/A/A Structure

SUP 9017 + 30%

SUP 9017 + 30%

SUP 9017 + 30%

SUP 9017 + 30%

SUP 9017 + 30%

SUP 9017 + 30%

SUP 9017 + 30%

SUP 9017 + 30%

No conditions were taken due to time limitations. We couldn't get the resin to extrude and on a scale. SUP 9017 will be explored further at a later date.

Additive PMA

7/16-72

7/16-72

CONFIDENTIAL

SIGNED

DATE

July 16, 1972

UNDERSTOOD AND WITNESSED

DATE

July 16, 1972

No 239363

B